

**COATING FILM HAVING PHOTOCATALYST ACTIVITY AND COMPOSITION FORM:  
SAME COATING FILM**

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**Abstract of JP9328336**

**PROBLEM TO BE SOLVED:** To obtain a composition capable of forming a coating film excellent in photocatalytic activity, mechanical strength and chemical resistance only by directly applying to a substrate without requiring pretreatment by using a specific composition.

**SOLUTION:** This composition contains (A) TiO<sub>2</sub> fine particles having <100nm average particle diameter, (B) element-containing compound and (C) a Si element-containing compound, and a weight ratio of the component A to the component C expressed in terms of a weight ratio of the component A: (the component B expressed in terms of ZrO<sub>2</sub>):(the component C expressed in terms of SiO<sub>2</sub>) is 1:(0.02 to 0.5):(0.2-2.5). A tetraalkoxide, an acetylacetoxylate compound, an alkoxyacetylacetone chelate compound or an acetate compound of Zr is employed as the component B. An alkoxysilane compound, chlorosilane compound, an isocyanato silane compound or its hydrolyzate is exemplified as the component C. This coating film is obtained by directly applying the composition to the substrate and heat-treating the composition.

ACRYLIC FILM FORMATION APPARATUS

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[Claim(s)]

[Claim 1] (1) Mean particle diameter is less than 100nm TiO<sub>2</sub>. Constituent whose weight ratio [ as opposed to (1) including a particle, (2) Zr element content compound, and (3) Si element content compound ] of (2) and (3) is (1):(ZrO<sub>2</sub> (2) of conversion):(SiO<sub>2</sub> (3) of conversion) =1:0.02-0.5:0.2-2.5.

[Claim 2] The manufacture approach of a coat of being the manufacture approach of a coat of having the photocatalyst activity formed in the base material, and performing heat treatment after applying the constituent of claim 1 to a direct base material and of having photocatalyst activity.

[Claim 3] The base material which has the coat formed using the constituent of claim 1.

[Claim 4] The base material of claim 3 whose thickness of a coat is 30-300nm.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention gives the resolvability of dirt, fog resistance, deodorization nature, antifungal nature, and antibacterial to various base materials, such as glass, plastics, a metal, and ceramics, and relates to the constituent for forming the photocatalyst activity coat which can use energy, such as sunlight and a fluorescent lamp, effectively, and this coat.

[0002]

[Description of the Prior Art] The antifouling property of building materials, such as indoor and outdoor glass, outer wall material, and a tile, antifungal nature, antibacterial, fog resistance, etc. are called for with the deodorization nature in indoor space with actualization of an environmental problem etc. Moreover, the same property has been required also about components, such as not only a building material but home electronics, office supplies, various cars, etc.

[0003] As a conventional technique over such a demand, it is TiO<sub>2</sub>. Forming the semi-conductor photocatalyst matter represented in a base material front face by conventionally well-known approaches, such as a spray method, the spin method, a dip method, and a spatter, was proposed (JP,6-278241,A).

[0004] However, since catalytic activity, a mechanical strength, and its chemical resistance of the coat formed with the conventional technique were insufficient, while in use, catalytic activity falls or gets damaged and it could not be satisfied from a practical viewpoint.

[0005] Moreover, since the coat by which the conventional proposal is made had the large refractive index of the film, when the coat was formed on transparent materials, such as glass, the strong interference fringe occurred and it had left the problem to design nature. Furthermore, in order to raise photocatalyst activity, the conventional proposal had prepared interlayers, such

as SiO<sub>2</sub> film, between the base material and the photocatalyst layer, and was disadvantageous also from viewpoints, such as cost.

[0006]

[Problem(s) to be Solved by the Invention] This invention aims at offer of the base material which has the coat which has the photocatalyst activity formed using the constituent for coat formation and this constituent which have the photocatalyst activity which can form the coat excellent in photocatalyst activity, a mechanical strength, and chemical resistance only by not needing special pretreatment of preparing an interlayer but applying to a base material directly, its manufacture approach, and this coat.

[0007]

[Means for Solving the Problem] For this invention, (1) mean particle diameter is less than 100nm TiO<sub>2</sub>. Particle (henceforth a compound (1)), (2) Zr element content compound (henceforth a compound (2)), and (3) Si element content compound (It is also hereafter called a compound (3)) It contains and the weight ratio of (2) and (3) to (1) offers the constituent which is (1):(ZrO<sub>2</sub> (2) of conversion):(SiO<sub>2</sub> (3) of conversion) =1:0.02-0.5:0.2-2.5.

[0008] The compound (1) used for this invention is an indispensable component for discovering catalytic activity, and is a particle with a mean particle diameter of less than 100nm. TiO<sub>2</sub> Although there is especially no limit in the configuration of a particle, it is desirable at the point that the thing of a globular shape and a needlelike gestalt raises membranous compactness, and has a mechanical strength raised.

[0009] Moreover, by 100nm or more, as for the mean particle diameter of a particle, a membranous appearance (especially transparency) and physical properties good in respect of a mechanical strength are not acquired. Moreover, the viewpoint of catalytic activity to TiO<sub>2</sub> The anatase mold of a crystalline form is desirable.

[0010] One of the descriptions of this invention is TiO<sub>2</sub>. It is in having used the ingredient which atomized beforehand as a source. This thing is TiO<sub>2</sub> which pyrolyzes various titanium compounds (for example, various titanium chelate compound, such as a titanium alkoxide, a titanium acetylacetone compound, and a titanium octylene glycol compound etc.), and is obtained. Compared with the film, the balance of catalytic activity and a mechanical strength is excellent. This reason is guessed as follows.

[0011] TiO<sub>2</sub> In order that a mechanical strength may be secured according to the chain structure of a particle and the clearance between particles may contribute the film using a particle to pore formation, membranous surface area increases as a result and catalytic activity is considered to become high. On the other hand, since the pyrolysis of the film which pyrolyzed various titanium compounds is carried out and many volatilization parts exist, it applies to membranous compactness that it is hard to take the chain structure of a titanium compound, and it is thought

that a mechanical strength cannot discover photocatalyst activity easily even if so so discovered.

[0012] The compound (2) used for this invention and (3) are the indispensable components for raising membranous endurance, i.e., a mechanical strength, and chemical resistance by leaps and bounds. A compound (2) and (3) are the compounds containing Zr element and Si element, respectively, and they are ZrO<sub>2</sub> and SiO<sub>2</sub> in the case of a heat treatment process. It is the compound which can serve as a component.

[0013] As a compound (2), a zirconium tetra-alkoxide, a zirconium acetylacetone chelate compound, a zirconium alkoxy acetylacetone chelate compound, a zirconium acetate compound, etc. are mentioned.

[0014] concrete -- Zr (acac) -- four -- Zr -- (OR) -- four -- Zr (acac) -- (OR) -- three -- Zr (acac) -- two 2 and Zr (acac)<sub>3</sub> (OR) and ZrO (OC two H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> etc. -- it can illustrate. here -- acac -- C five H<sub>7</sub>O<sub>2</sub> an acetylacetone -- OR -- OC three H<sub>7</sub> and OC four H<sub>9</sub> etc. -- an alkoxy group is meant.

[0015] Moreover, as a compound (3), an alkoxy silane compound, a chlorosilane compound, isocyanate silane compounds, or those partial hydrolysis products are mentioned.

[0016] concrete -- Si -- (OR) -- four -- R -- one -- Si -- (OR) -- three -- R -- one -- R -- two -- Si -- (OR) -- two -- Si (NCO) -- four -- R -- one -- Si (NCO) -- three -- R -- one -- R -- two -- Si (NCO) -- two -- ethyl silicate -- 40 (that whose average degree of polymerization it is the partial hydrolysis product of a tetra-ethoxy silane, and is 5) -- etc. -- and -- those -- partial hydrolysis -- a product -- etc. -- it can illustrate . It is R1 and R2 here. An alkyl group is meant.

[0017] A compound (2) and (3) may not be limited to one sort of ingredients, but they may be the mixture of two or more sorts of compounds, and a cohydrolysis product.

[0018] The weight ratios [(ZrO<sub>2</sub> of a compound (2) equivalent weight) /(1)] to the compound (1) of a compound (2) are 0.02-0.5. When [ than 0.5 ] more [ the effectiveness of addition, a mechanical strength and chemical resistance will not be discovered if fewer than 0.02, and ], it is for causing the fall of photocatalyst activity and the adhesion to the base material of a coat.

[0019] The weight ratios [(SiO<sub>2</sub> of a compound (3) equivalent weight) /(1)] to the compound (1) of a compound (3) are 0.2-2.5. Less than in 0.2, when [ than 2.5 ] more [ the addition effectiveness is not discovered, and a mechanical strength and chemical resistance do not improve and ], it is for photocatalyst activity to fall.

[0020] Moreover, although a mechanical strength and chemical resistance improve so so even if it uses a compound (2) and (3) by each independent one, effectiveness which is seen when a compound (2) and (3) live together like this invention is not expectable.

[0021] Although especially the weight ratio of a compound (2) to a compound (3) is not limited (ZrO<sub>2</sub> of a compound (2) equivalent weight), as for / (SiO<sub>2</sub> of a compound (3) equivalent weight), it is desirable that it is 0.05-0.7. It is for the synergistic effect of a compound (2) and a

compound (3) to be hard to be acquired, for the bad influence of a compound (2) to begin to appear in 0.7 \*\*, namely, for the adhesion of the film to a base material to come to fall less than in 0.05.

[0022] As the method of application of the constituent of this invention, approaches, such as a spray coating cloth, spin coat spreading, flexographic printing spreading, screen-stencil spreading, DIP coat spreading, brush coating, and flow coat spreading, are used.

[0023] If the constituent of this invention is used, it will be SiO<sub>2</sub> between a coat and a base material like the conventional technique. It is not necessary to prepare an interlayer like the film, and the coat which has the photocatalyst activity and the mechanical strength which applied to the direct base material and were excellent in heat-treating, and chemical resistance is obtained. That is, special pretreatment is considered to be an unnecessary and advantageous approach also in cost. However, pretreating for a certain purpose is convenient.

[0024] The range of temperature for 5 - 60 minutes is [ the heat treatment conditions in this invention / 80-700 degrees C and time amount ] desirable, and a temperature profile can set up according to the purpose suitably. This invention has the description that a property manifestation is possible also for low temperature treatment as mentioned above.

[0025] As for the thickness of a coat, it is desirable to set it as 30-300nm. It is for photocatalyst activity sufficient in less than 30nm to be hard to be acquired, and for a blemish etc. to come to be conspicuous since a mechanical strength falls in 300nm \*\*, and for a practical use property to fall.

[0026] Especially the base material in this invention is not limited, but can use glass, the ceramics, plastics, metals and those complex, and a layered product. The front face of the quality of the material where the base materials itself, such as a front face (for example, glass front face in which the sol gel film, the spatter film, the CVD film, the vacuum evaporationo film, etc. were prepared) by which surface treatment was carried out, differ is sufficient as the front face of a base material also on the front face of the base material itself. Especially the configuration of a base material may not be limited, but a plane thing is sufficient as it, and it is good in the configuration of the arbitration according to the purpose. [ of the whole surface or the thing which has curvature partially ]

[0027]

[Example] The evaluation approach used in the example and the example of a comparison is as follows.

[0028] Photocatalyst activity: The photolysis reaction rate of the acetaldehyde which is the offensive odor component of tobacco was evaluated. An experiment pays the sample of 50mm angle to the 3l. square shape coil made from a quartz, and introduces an acetaldehyde steam into a coil, and the ultraviolet-rays reinforcement in a sample side is 2 1.5mW/cm. The black light

was irradiated from the quartz coil exterior at the sample so that it might become, the decrement of an acetaldehyde was measured by the gas chromatograph, and the rate of acetaldehyde decomposition was found. Catabolic rate was expressed by unit time amount and the weight decrement per unit area [mug/(h-cm<sup>2</sup>)].

[0029] Abrasion resistance: The Taber testing machine performed 500g of loads, and 1000 wear, and the variation of the haze before and behind a trial was calculated.

[0030] Appearance quality: The existence of an interference fringe was checked for the appearance of the obtained test piece with the naked eye.

[0031] Fog resistance: It divided into initial fog resistance and durable fog resistance, and the following approach estimated. Initial fog resistance was observed [ whether a breath is blown upon a sample and cloudiness occurs, and ] with the naked eye. Durable fog resistance evaluated the obtained test piece by the same approach as initial fog resistance after immersion in 60-degree C warm water on the 3rd. In fog resistance evaluation, O bloomed cloudy, and was not generated, but x bloomed cloudy, and it considered as generating.

[0032] Chemical resistance: Change was observed after 24-hour immersion in the 0.1-N NaOH water solution at the membranous appearance with the naked eye.

[0033] In 56g (anatase TiO<sub>2</sub> the particle of 10 % of the weight, mean particle diameter of 60nm) of ethanol distribution solutions of a [example 1] titanium oxide particle, ethanol 478g, tetramethoxy silane 12.5g, and zirconium TORIBUTOKISHI acetylacetone Zr(C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 2.3g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent 1 was obtained. In this case, SiO<sub>2</sub> Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is 0.87 and is ZrO<sub>2</sub>. Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is set to 0.09.

[0034] One cc of processing agents 1 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 86nm. The evaluation result of this test piece is shown in Table 1 (following, the same).

[0035] The 12.5g tetramethoxy silane was changed into 12.0g ethyl silicate 40 in the [example 2] example 1, and also the same approach as an example 1 created and estimated the test piece.

[0036] Mean particle diameter was changed into the 33nm thing, and also the test piece was created and the same approach as an example 1 estimated the titanium oxide particle with a mean particle diameter [ of the [example 3] example 1 ] of 60nm.

[0037] In 56g (anatase TiO<sub>2</sub> the particle of 10 % of the weight, mean particle diameter of 60nm) of ethanol distribution solutions of a [example 4] titanium oxide particle, ethanol 330g, tetramethoxy silane 4.3g, and Zr(C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 2.5g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent 4 was obtained. In

this case, SiO<sub>2</sub> Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is 0.29 and is ZrO<sub>2</sub>. Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is set to 0.10.

[0038] One cc of processing agents 4 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 86nm.

[0039] In 56g (anatase TiO<sub>2</sub> the particle of 10 % of the weight, mean particle diameter of 60nm) of ethanol distribution solutions of a [example 5] titanium oxide particle, ethanol 395g, tetramethoxy silane 6.5g, and Zr(C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 5.0g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent 5 was obtained. In this case, SiO<sub>2</sub> Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is 0.45 and is ZrO<sub>2</sub>. Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is set to 0.20.

[0040] One cc of processing agents 5 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 86nm.

[0041] It sets in the [example 6] example 5, and is 5.0g Zr (C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub>. 5.96g zirconium tetra-acetylacetone was used instead, and also the same approach as an example 5 created and estimated the test piece.

[0042] In 56g (anatase TiO<sub>2</sub> the particle of 10 % of the weight, mean particle diameter of 60nm) of ethanol distribution solutions of the [example 1 of comparison] titanium oxide particle, ethanol 455g and tetramethoxy silane 12.5g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent R1 was obtained.

[0043] One cc of processing agents R1 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 83nm.

[0044] In 56g (anatase TiO<sub>2</sub> 10 % of the weight mean particle diameter of 60nm of particles) of ethanol distribution solutions of the [example 2 of comparison] titanium oxide particle, ethanol 446g and Zr(C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 22.0g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent R2 was obtained.

[0045] One cc of processing agents R2 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 86nm.

[0046] Ethanol 224g was added in 56g (anatase TiO<sub>2</sub> the particle of 10 % of the weight, mean

particle diameter of 60nm) of ethanol distribution solutions of the [example 3 of comparison] titanium oxide particle. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent R3 was obtained.

[0047] One cc of processing agents R3 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 92nm.

[0048] In 56g (anatase TiO<sub>2</sub> 10 % of the weight mean particle diameter of 60nm of particles) of ethanol distribution solutions of the [example 4 of comparison] titanium oxide particle, ethanol 478g, tetramethoxy silane 1.43g, and Zr(C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 0.3g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent R4 was obtained. In this case, SiO<sub>2</sub> Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is 0.10 and is ZrO<sub>2</sub>. Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is set to 0.01.

[0049] One cc of processing agents R4 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 85nm.

[0050] In 28g (anatase TiO<sub>2</sub> 10 % of the weight mean particle diameter of 60nm of particles) of ethanol distribution solutions of the [example 5 of comparison] titanium oxide particle, ethanol 638g, tetramethoxy silane 21.6g, and Zr(C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 12.6g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent R5 was obtained. In this case, SiO<sub>2</sub> Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is 3.01 and is ZrO<sub>2</sub>. Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is set to 1.00.

[0051] One cc of processing agents R5 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 78nm.

[0052] To [example 6 of comparison] tetrabutoxytitanium 23.8g, ethanol 478g, tetramethoxy silane 12.5g, and Zr(C five H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 2.3g were added. The above-mentioned solution was agitated at 25 degrees C for 1 hour, and the processing agent R6 was obtained. In this case, SiO<sub>2</sub> Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is 0.87 and is ZrO<sub>2</sub>. Equivalent weight / TiO<sub>2</sub> Equivalent weight = it is set to 0.09.

[0053] One cc of processing agents R6 was dropped at the glass substrate washed beforehand, spin coat spreading was carried out, it heat-treated for 5 minutes at 650 degrees C after that, and the test piece was obtained. The thickness of the coat with which the piece of an exam was prepared was 77nm.

[0054]

[Table 1]

実施例	光触媒活性	耐磨耗性	耐薬品性	防曇性	
				初期	耐久
実施例 1	12.3	2.1	変化なし	○	○
実施例 2	12.0	2.4	変化なし	○	○
実施例 3	11.8	1.8	変化なし	○	○
実施例 4	21.0	3.6	変化なし	○	○
実施例 5	16.5	2.7	変化なし	○	○
比較例 1	9.8	5.6	剥離	○	×
比較例 2	8.8	4.9	剥離	○	×
比較例 3	15.6	剥離	剥離	○	○
比較例 4	16.5	剥離	剥離	○	○
比較例 5	4.8	剥離	変化なし	×	×
比較例 6	6.5	剥離	変化なし	×	×

[0055]

[Effect of the Invention] By using the constituent of this invention, special pretreatment of preparing an interlayer is not needed but the coat excellent in photocatalyst activity, a mechanical strength, and chemical resistance can be formed only by applying to a base material directly.

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(54)【発明の名称】 光触媒活性を有する被膜とそれを形成する組成物

(57)【要約】

【課題】光触媒活性、機械的強度及び耐薬品性が優れた被膜を容易に形成できる組成物と、該組成物を用いて形成した被膜の提供。

【解決手段】(1)平均粒子径が100nm未満のTiO<sub>2</sub>微粒子と、(2)Zr元素含有化合物と、及び(3)Si元素含有化合物とを含み、かつ酸化物換算の重量比が、(2)/(1)で0.02~0.5、(3)/(1)で0.2~2.5である組成物、該組成物を用いて形成した被膜。

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## 【特許請求の範囲】

【請求項1】(1) 平均粒子径が100nm未満のTiO<sub>2</sub>微粒子と、(2) Zr元素含有化合物と、(3) Si元素含有化合物とを含み、(1)に対する(2)、(3)の重量比が、(1)：(ZrO<sub>2</sub>換算の(2))：(SiO<sub>2</sub>換算の(3))=1:0.02～0.5:0.2～2.5である組成物。

【請求項2】基材に形成された光触媒活性を有する被膜の製造方法であって、請求項1の組成物を直接基材に塗布した後、熱処理を施す、光触媒活性を有する被膜の製造方法。

【請求項3】請求項1の組成物を用いて形成された被膜を有する基材。

【請求項4】被膜の膜厚が30～300nmである請求項3の基材。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、ガラス、プラスチック、金属、セラミックスなどの各種基材に汚れの分解性、防曇性、脱臭性、防かび性、抗菌性を付与し、太陽光、蛍光灯等のエネルギーを有効利用可能な光触媒活性被膜、及び該被膜を形成するための組成物に関する。

## 【0002】

【従来の技術】環境問題等の顕在化に伴い、室内空間における脱臭性とともに室内及び室外のガラス、外壁材、タイル等の建築材料の防汚性、防かび性、抗菌性、防曇性等が求められている。また、建築材料に限らず家電製品、事務用品、各種車両等の構成材料に関して同様の特性が要求されてきている。

【0003】こうした要求に対する従来技術としてはTiO<sub>2</sub>に代表される半導体光触媒物質を、スプレー法、スピノ法、ディップ法、スパッタ法等の従来公知の方法で基材表面に形成することが提案されていた(特開平6-278241)。

【0004】しかし、従来技術で形成した被膜は、触媒活性、機械的強度及びその耐薬品性が不充分であったため、使用中に触媒活性が低下したり、傷ついたりして実用的観点からは満足しえなかった。

【0005】また、従来提案されている被膜は、その膜の屈折率が大きいためガラス等の透明材料上に被膜を形成すると強い干渉縞が発生し意匠性に問題を残していた。さらに、従来の提案は光触媒活性を高めるためには、基材と光触媒層の間にSiO<sub>2</sub>膜等の中間層を設けており、コスト等の観点からも不利なものであった。

## 【0006】

【発明が解決しようとする課題】本発明は中間層を設ける等の特別な前処理を必要とせず、基材に直接塗布するだけで光触媒活性、機械的強度及び耐薬品性が優れた被膜が形成可能な光触媒活性を有する被膜形成用組成物、該組成物を用いて形成した光触媒活性を有する被膜とそ

の製造方法、及び該被膜を有する基材の提供を目的とする。

## 【0007】

【課題を解決するための手段】本発明は、(1)平均粒子径が100nm未満のTiO<sub>2</sub>微粒子(以下、化合物(1)ともいう)と、(2)Zr元素含有化合物(以下、化合物(2)ともいう)と、(3)Si元素含有化合物(以下、化合物(3)ともいう)とを含み、(1)に対する(2)、(3)の重量比が、(1)：(ZrO<sub>2</sub>換算の(2))：(SiO<sub>2</sub>換算の(3))=1:0.02～0.5:0.2～2.5である組成物を提供する。

【0008】本発明に用いる化合物(1)は触媒活性を発現するための必須成分であり、平均粒子径100nm未満の微粒子である。TiO<sub>2</sub>微粒子の形状に特に制限はないが、球状、針状形態のものが膜の緻密性を向上させ、機械的強度を高められる点で好ましい。

【0009】また、微粒子の平均粒子径は100nm以上では膜の外観(特に透明性)、機械的強度の点で良好な物性が得られない。また、触媒活性の観点からTiO<sub>2</sub>の結晶形態はアナターゼ型が好ましい。

【0010】本発明の特徴の1つはTiO<sub>2</sub>源としてあらかじめ微粒子化した材料を用いたことにある。このものは各種チタン化合物、(例えば、チタンアルコキシド、チタンアセチルアセトン化合物、チタンオクチレングリコール化合物等の各種チタンキレート化合物等)を熱分解して得られるTiO<sub>2</sub>膜に比べ、触媒活性及び機械的強度のバランスが優れている。この理由は以下のように推察される。

【0011】TiO<sub>2</sub>微粒子を用いた膜は微粒子の連鎖構造により、機械的強度が確保され、かつ微粒子間の隙間が細孔形成に寄与するため、結果として膜の表面積が増大し触媒活性が高くなると考えられる。一方、各種チタン化合物を熱分解した膜は、熱分解されて揮発部分が多く存在するため、チタン化合物の連鎖構造がとりにくく膜の緻密性にかけ、光触媒活性はそこそこ発現しても機械的強度が発現しにくいと考えられる。

【0012】本発明に用いる化合物(2)、(3)は膜の耐久性、すなわち、機械的強度及び耐薬品性を飛躍的に高めるための必須成分である。化合物(2)、(3)はそれぞれZr元素、Si元素を含有する化合物であって、熱処理工程の際に、ZrO<sub>2</sub>、SiO<sub>2</sub>成分となる化合物である。

【0013】化合物(2)としては、ジルコニウムテトラアルコキシド、ジルコニウムアセチルアセトンキレート化合物、ジルコニウムアルコキシアセチルアセトンキレート化合物、ジルコニウムアセテート化合物等が挙げられる。

【0014】具体的には、Zr(acac)<sub>4</sub>、Zr(OR)<sub>4</sub>、Zr(acac)(OR)<sub>3</sub>、Zr(acac)<sub>3</sub>等が挙げられる。

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$\text{ac}_2(\text{OR})_2$ 、 $\text{Zr}(\text{acac})_3(\text{OR})$ 、 $\text{ZrO}(\text{OC}_2\text{H}_3\text{O}_2)_2$ 等が例示できる。ここで $\text{ac}$ は $\text{C}_5\text{H}_7\text{O}_2$ のアセチルアセトンを、 $\text{OR}$ は $\text{OC}_3\text{H}_7$ 、 $\text{OC}_4\text{H}_9$ 等のアルコキシ基を意味する。

【0015】また、化合物(3)としては、アルコキシラン化合物、クロロシラン化合物、イソシアネートシラン化合物、又はそれらの部分加水分解生成物等が挙げられる。

【0016】具体的には、 $\text{Si}(\text{OR})_4$ 、 $\text{R}^1\text{Si}(\text{OR})_3$ 、 $\text{R}^1\text{R}^2\text{Si}(\text{OR})_2$ 、 $\text{Si}(\text{NCO})_4$ 、 $\text{R}^1\text{Si}(\text{NCO})_3$ 、 $\text{R}^1\text{R}^2\text{Si}(\text{NCO})_2$ 、エチルシリケート40(テトラエトキシシランの部分加水分解生成物であって平均重合度が5であるもの)等、及びそれらの部分加水分解生成物等が例示できる。ここで $\text{R}^1$ 、 $\text{R}^2$ はアルキル基を意味する。

【0017】化合物(2)、(3)は1種の材料に限定されず、2種以上の化合物の混合物、共加水分解生成物であってもよい。

【0018】化合物(2)の化合物(1)に対する重量比[(化合物(2)の $\text{ZrO}_2$ 換算重量)/(1)]は0.02~0.5である。0.02より少ないと添加の効果、機械的強度及び耐薬品性が発現せず、0.5より多いと光触媒活性及び被膜の基材への密着性の低下を招くためである。

【0019】化合物(3)の化合物(1)に対する重量比[(化合物(3)の $\text{SiO}_2$ 換算重量)/(1)]は0.2~2.5である。0.2未満では添加効果が発現せず、機械的強度及び耐薬品性が向上せず、2.5より多いと光触媒活性が低下するためである。

【0020】また、化合物(2)、(3)を各単独で用いてもそこそこ機械的強度及び耐薬品性は向上するが、本発明のように化合物(2)、(3)が共存する場合にみられるような効果は期待できない。

【0021】化合物(3)に対する化合物(2)の重量比は特に限定されないが(化合物(2)の $\text{ZrO}_2$ 換算重量)/(化合物(3)の $\text{SiO}_2$ 換算重量)は、0.05~0.7であることが望ましい。0.05未満では化合物(2)及び化合物(3)の相乗効果が得られにくく、また、0.7超では化合物(2)の悪影響が出始め、すなわち、基材への膜の密着性が低下するようになるためである。

【0022】本発明の組成物の塗布方法としては、スプレー塗布、スピンドル塗布、フレキソ印刷塗布、スクリーン印刷塗布、ディップコート塗布、刷毛塗り、フローコート塗布等の方法が用いられる。

【0023】本発明の組成物を用いれば、従来技術のように被膜と基材との間に $\text{SiO}_2$ 膜のような中間層を設ける必要がなく、直接基材に塗布し、熱処理することで優れた光触媒活性、機械的強度及び耐薬品性を有する被膜が得られる。すなわち、特別な前処理が必要なくコスト

的にも有利な方法と考えられる。しかし、何らかの目的で前処理を施すことは支障ない。

【0024】本発明における熱処理条件は、温度は80~700°C、時間は5~60分の範囲が好ましく、温度プロファイルは適宜目的に応じて設定できる。本発明は上記のように低温処理でも特性発現可能であるという特徴を有する。

【0025】被膜の厚さは30~300nmに設定することが好ましい。30nm未満では充分な光触媒活性が得られにくく、また、300nm超では機械的強度が低下するため、傷等が目立つようになり実用特性が低下するためである。

【0026】本発明における基材は特に限定されず、ガラス、セラミックス、プラスチック、金属及びそれらの複合体、積層体が利用できる。基材の表面は、基材そのものの表面でも、表面処理された表面(例えば、ゾルゲル膜、スパッタ膜、CVD膜、蒸着膜等が設けられたガラス表面)などの基材そのものとは異なる材質の表面でもよい。基材の形状は特に限定されず、平面状のものでもよく、全面又は部分的に曲率を有するものなど、目的に応じた任意の形状でよい。

#### 【0027】

【実施例】実施例、比較例で用いた評価方法は次のとおりである。

【0028】光触媒活性：タバコの悪臭成分であるアセトアルデヒドの光分解反応速度を評価した。実験は50mm角の試料を3リットルの石英製角型反応管に入れ、アセトアルデヒド蒸気を反応管に導入し、試料面での紫外線強度が1.5mW/cm<sup>2</sup>となるように石英反応管外部から試料にブラックライトを照射し、アセトアルデヒドの減少量をガスクロマトグラフで測定してアセトアルデヒド分解の速度を求めた。分解速度は単位時間、単位面積当たりの重量減少量[ $\mu\text{g}/(\text{h} \cdot \text{cm}^2)$ ]で表現した。

【0029】耐磨耗性：テーパー試験機にて荷重500g、摩耗1000回を行い、試験前後のヘーズの変化量を求めた。

【0030】外観品質：得られた試験片の外観を肉眼で干渉縞の有無を確認した。

【0031】防疊性：初期防疊性と耐久防疊性に分けて次の方法で評価した。初期防疊性は息を試料に吹きかけ疊りが発生するか否か肉眼で観察した。耐久防疊性は、得られた試験片を60°Cの温水に3日浸漬後、初期防疊性と同様の方法で評価した。防疊性評価において、○は疊り発生せず、×は疊り発生、とした。

【0032】耐薬品性：0.1NのNaOH水溶液に24時間浸漬後、膜の外観に変化を肉眼で観察した。

【0033】【実施例1】酸化チタン微粒子のエタノール分散溶液(アナターゼ $\text{TiO}_2$ 微粒子10重量%、平均粒子径60nm)56gに、エタノール478g、テ

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トラメトキシシラン12.5g及びジルコニウムトリプトキシアセチルアセトネット $Zr(C_5H_7O_3)(OBu)_3$ 2.3gを添加した。上記溶液を25°Cで1時間攪拌し処理剤1を得た。この場合、 $SiO_2$ 換算重量/ $TiO_2$ 換算重量=0.87であり、 $ZrO_2$ 換算重量/ $TiO_2$ 換算重量=0.09となる。

【0034】あらかじめ洗浄されたガラス基板に処理剤1を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は86nmであった。この試験片の評価結果を表1に示す(以下、同様)。

【0035】[実施例2]実施例1において12.5gのテトラメトキシシランを12.0gのエチルシリケート40に変更した他は実施例1と同様の方法で試験片を作成し評価した。

【0036】[実施例3]実施例1の平均粒子径60nmの酸化チタン微粒子を平均粒子径を33nmのものに変更した他は実施例1と同様の方法で試験片を作成し評価した。

【0037】[実施例4]酸化チタン微粒子のエタノール分散溶液(アナターゼ $TiO_2$ 微粒子10重量%、平均粒子径60nm)56gに、エタノール330g、テトラメトキシシラン4.3g及び $Zr(C_5H_7O_3)(OBu)_3$ 2.5gを添加した。上記溶液を25°Cで1時間攪拌し処理剤4を得た。この場合、 $SiO_2$ 換算重量/ $TiO_2$ 換算重量=0.29であり、 $ZrO_2$ 換算重量/ $TiO_2$ 換算重量=0.10となる。

【0038】あらかじめ洗浄されたガラス基板に処理剤4を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は86nmであった。

【0039】[実施例5]酸化チタン微粒子のエタノール分散溶液(アナターゼ $TiO_2$ 微粒子10重量%、平均粒子径60nm)56gに、エタノール395g、テトラメトキシシラン6.5g及び $Zr(C_5H_7O_3)(OBu)_3$ 5.0gを添加した。上記溶液を25°Cで1時間攪拌し処理剤5を得た。~~並びに~~ $SiO_2$ 換算重量/ $TiO_2$ 換算重量=0.45であり、 $ZrO_2$ 換算重量/ $TiO_2$ 換算重量=0.20となる。

【0040】あらかじめ洗浄されたガラス基板に処理剤5を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は86nmであった。

【0041】[実施例6]実施例5において5.0gの $Zr(C_5H_7O_3)(OBu)_3$ のかわりに5.96gのジルコニウムテトラアセチルアセトネットを用いた他は実施例5と同様の方法で試験片を作成し評価した。

【0042】[比較例1]酸化チタン微粒子のエタノール分散溶液(アナターゼ $TiO_2$ 微粒子10重量%、平均粒子径60nm)56gに、エタノール455g、テ

トラメトキシシラン12.5gを添加した。上記溶液を25°Cで1時間攪拌し処理剤R1を得た。

【0043】あらかじめ洗浄されたガラス基板に処理剤R1を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は83nmであった。

【0044】[比較例2]酸化チタン微粒子のエタノール分散溶液(アナターゼ $TiO_2$ 微粒子10重量%、平均粒子径60nm)56gに、エタノール446g、 $Zr(C_5H_7O_3)(OBu)_3$ 22.0gを添加した。上記溶液を25°Cで1時間攪拌し処理剤R2を得た。

【0045】あらかじめ洗浄されたガラス基板に処理剤R2を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は86nmであった。

【0046】[比較例3]酸化チタン微粒子のエタノール分散溶液(アナターゼ $TiO_2$ 微粒子10重量%、平均粒子径60nm)56gに、エタノール224gを添加した。上記溶液を25°Cで1時間攪拌し処理剤R3を得た。

【0047】あらかじめ洗浄されたガラス基板に処理剤R3を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は92nmであった。

【0048】[比較例4]酸化チタン微粒子のエタノール分散溶液(アナターゼ $TiO_2$ 微粒子10重量%、平均粒子径60nm)56gに、エタノール478g、テトラメトキシシラン1.43g及び $Zr(C_5H_7O_3)(OBu)_3$ 0.3gを添加した。上記溶液を25°Cで1時間攪拌し処理剤R4を得た。この場合、 $SiO_2$ 換算重量/ $TiO_2$ 換算重量=0.10であり、 $ZrO_2$ 換算重量/ $TiO_2$ 換算重量=0.01となる。

【0049】あらかじめ洗浄されたガラス基板に処理剤R4を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は85nmであった。

【0050】[比較例5]酸化チタン微粒子のエタノール分散溶液(アナターゼ $TiO_2$ 微粒子10重量%、平均粒子径60nm)28gに、エタノール638g、テトラメトキシシラン21.6g及び $Zr(C_5H_7O_3)(OBu)_3$ 12.6gを添加した。上記溶液を25°Cで1時間攪拌し処理剤R5を得た。この場合、 $SiO_2$ 換算重量/ $TiO_2$ 換算重量=3.01であり、 $ZrO_2$ 換算重量/ $TiO_2$ 換算重量=1.00となる。

【0051】あらかじめ洗浄されたガラス基板に処理剤R5を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は78nmであった。

【0052】[比較例6]テトラブトキシチタン23.

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8 gに、エタノール478 g、テトラメトキシシラン12.5 g及びZr (C<sub>5</sub>H<sub>7</sub>O<sub>3</sub>) (OBu)<sub>3</sub> 2.3 gを添加した。上記溶液を25°Cで1時間攪拌し処理剤R6を得た。この場合、SiO<sub>2</sub> 換算重量/TiO<sub>2</sub> 換算重量 = 0.87であり、ZrO<sub>2</sub> 換算重量/TiO<sub>2</sub> 換算重量 = 0.09となる。

【0053】あらかじめ洗浄されたガラス基板に処理剤R6を1cc滴下し、スピンドルコート塗布し、その後650°Cで5分間熱処理し試験片を得た。本試験片の設けられた被膜の膜厚は77 nmであった。

## 【0054】

【表1】

実施例	光触媒活性	耐磨耗性	耐薬品性	防曇性	
				初期	耐久
実施例1	12.3	2.1	変化なし	○	○
実施例2	12.0	2.4	変化なし	○	○
実施例3	11.8	1.8	変化なし	○	○
実施例4	21.0	3.6	変化なし	○	○
実施例5	16.5	2.7	変化なし	○	○
比較例1	9.8	5.6	剥離	○	×
比較例2	8.8	4.9	剥離	○	×
比較例3	15.6	剥離	剥離	○	○
比較例4	16.5	剥離	剥離	○	○
比較例5	4.8	剥離	変化なし	×	×
比較例6	6.5	剥離	変化なし	×	×

## 【0055】

【発明の効果】本発明の組成物を用いることにより、中間層を設ける等の特別な前処理を必要とせず、基材に直

接塗布するだけで光触媒活性、機械的強度及び耐薬品性が優れた被膜を形成できる。

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